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Diffusion of platinum, vanadium and manganese in Ni_3Al phase under high pressure

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Diffusion of platinum, vanadium, and manganese in the Ni_3Al phase is investigated under high pressure. Platinum atoms occupy cubic face centred sites (α) in the $L1_2$ ordering structure. Vanadium atoms occupy cubic corner sites (β). Manganese atoms occupy both sites. Activation volumes ΔV for diffusion of these diffusing atoms to the molar volume of the Ni_3Al phase V_0 are as follows:

$$\Delta V/V_0 \text{ for Pt: } 0.75, \quad V\text{: } 0.97\text{–}1.08, \quad \text{Mn: } 1.01\text{–}1.03$$

These values mean that the diffusion of platinum is mediated by single vacancies, that of vanadium is done by divacancies or other complex mechanisms, and that of manganese via single vacancies plus other mechanisms. © *1999 Kluwer Academic Publishers*

1. Introduction

Heat resisting nickel base super alloys contain an intermetallic Ni_3Al phase (γ') in an fcc matrix [1]. The intermetallic Ni_3Al phase increases its strength at higher temperatures and show a maximum strength at about 970–110 K [2]. The Ni_3Al phase has an $L1_2$ ordering structure [3] in which nickel atoms occupy cubic face centred sites (α) and aluminium atoms corner sites (β). A nickel atom has eight nearest neighbour nickel sites and can jump from a nickel atom site to an adjacent nickel atom sites via an atom vacancy without introducing disorder. On the other hand, an aluminium atom has no adjacent nearest neighbour aluminium site. As seen in Fig. 1 [4], platinum atoms substitute for nickel atoms, vanadium atoms for aluminium, and manganese atoms for both sites because a platinum solubility lobe expands to a constant aluminium concentration, and a vanadium solubility lobe to a constant nickel concentration. That of manganese expands to a middle direction.

Therefore, authors attempt to measure activation volumes and activation energies for the diffusion of those elements in the Ni_3Al phase in order to estimate the diffusion mechanisms.

2. Experimentals

Four alloys were prepared from aluminium (99.99 mass %), nickel (99.99 mass %), platinum (99.9 mass %), vanadium (99.9 mass %), and manganese (99.9 mass %) in a vacuum induction melting furnace. After homogenization at 1523 K for 30×3.6 ks in argon gas. These cast alloy ingots were machined to 4 mm in diameter and 2.5 mm in height disks for diffusion under high pressure, and cut about 5 mm × 5 mm × 1.5 mm blocks for diffusion at 90 kPa. Diffusion surfaces were polished metallographically with the mixture of 0.3 μm alumina powders and water. The average grain diameter of these alloys was about 1.2 mm. A diffusion couple disks was placed in a high pressure cell as shown in Fig. 2. The high pressure cell was pressed by six cubic anvils from six directions of the top and bottom, right and left, front and rear. The six cubic anvils were made from the sintered mixture of tungsten carbide and cobalt powders. The diffusion couple was diffusion annealed under high pressure. The alloy block were assembled as three kinds of diffusion couples by being clamped with a stainless holder. The diffusion couples were sealed in quartz capsules with Ar^+ 5% H_2 gas at 90 kPa and these couples were diffusion annealed. Table I shows the alloy compositions of diffusion couples.

After being diffusion annealing, the diffusion couple was cut parallel to the diffusion direction, and mechanically polished with the mixture of 0.3 μm alumina powders and water. The concentrations of aluminium, platinum vanadium and manganese were measured in an electron probe microanalyser. The intensities of K_α of these elements were converted into their concentrations by the ZAF method [5].

When the solute atom fraction N_i of an element i approaches to 0 in ternary i-j-k alloys, where i is platinum, vanadium or manganese, j aluminium, and k nickel. Two direct coefficients become equal to the impurity diffusion coefficients, and two indirect

TABLE I Terminal compositions of diffusion couples (at %)

Ni-24.9Al/Ni-24.5Al-2.07Pt
Ni-24.9Al/Ni-22.5Al-1.75V
Ni-24.9Al/Ni-22.2Al-1.88Mn

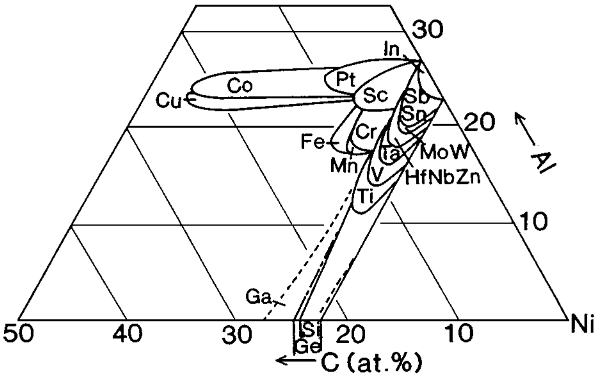

Figure 1 Schematic solubility lobes of various elements in Ni_3Al phase. *C* is concentrations of third elements.

coefficients to zero as follows [6]:

$$\lim_{N_i \to 0} D^k_{ii} = D^*_i(j-k) \qquad (1)$$

$$\lim_{N_i \to 0} D^k_{ij} = 0 \qquad (2)$$

where D^k_{ii} is the direct coefficient of i, D^k_{ij} the cross coefficient of i and $D^*_i(j-k)$ the impurity diffusion coefficient of i. By the extrapolation of platinum, vanadium, and manganese concentration dependencies of D^k_{ii} to zero concentration, the impurity diffusion coefficients of those three elements in the Ni_3Al phase are obtained. $D^k_{ii}(0)$ at the terminal zero concentration of i is obtained by the Hall method [7].

3. Results and discussions

Figs 3–5 show diffusion concentration profiles of aluminium, platinum, vanadium and manganese, where *X* is the diffusion distance from Matano interface and *t*

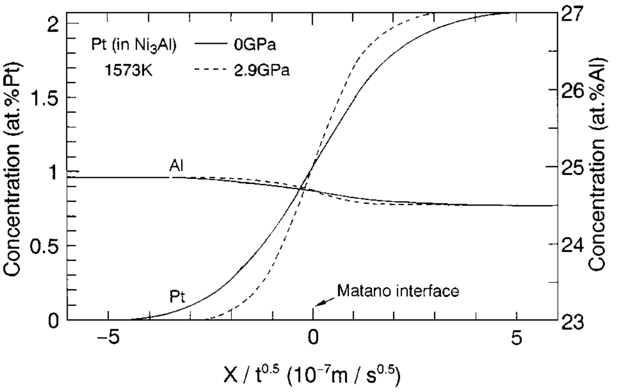

Figure 3 Concentration profiles of Al and Pt diffusion annealed at 1573 K for 108 ks (90 kPa) and 43.2 ks (2.9 GPa) where *t* is diffusion time, *X* diffusion distance from Matano interface.

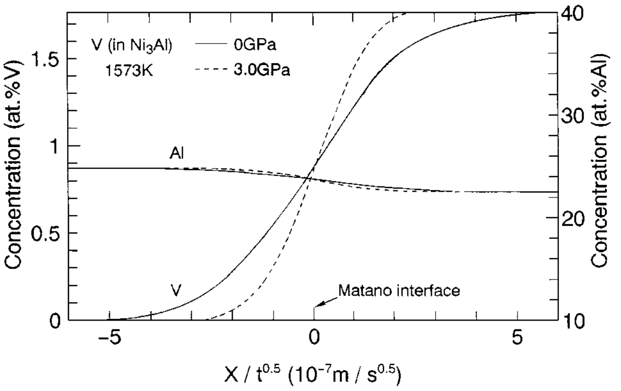

Figure 4 Concentration profiles of Al and V diffusion annealed at 1573 K for 61.2 ks (90 kPa) and 25.2 ks (3.0 GPa) where *t* is diffusion time, *X* diffusion distance from Matano interface.

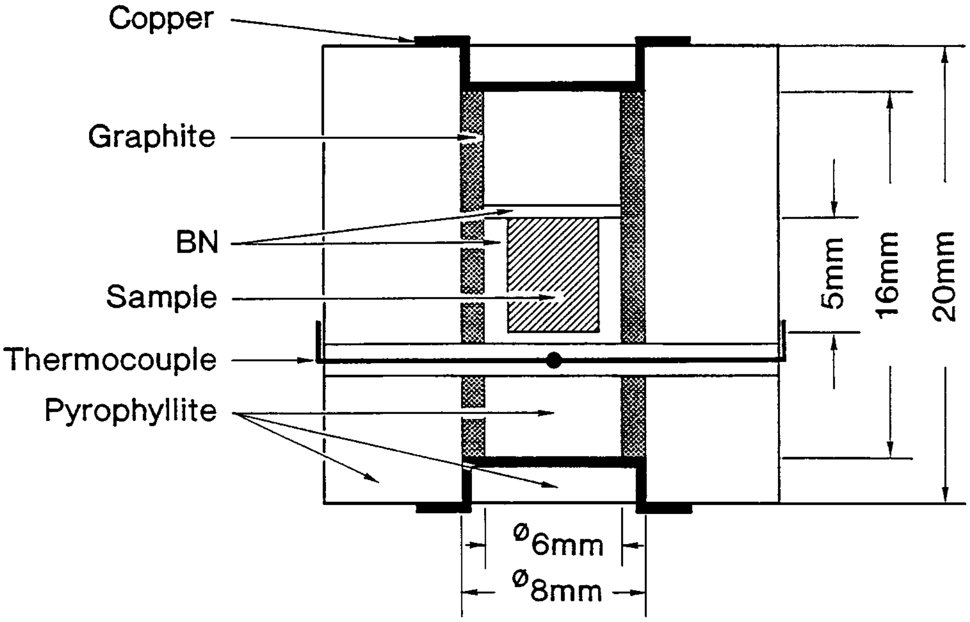

Figure 2 Section figure of high pressure cell which is pressed by cubic anvils from six direction, top and bottom, right and left, front and rear sides.

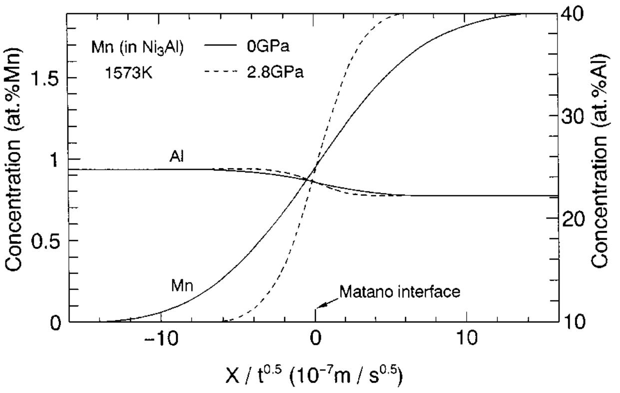

Figure 5 Concentration profiles of Al and Mn diffusion annealed at 1573 K for 9 ks (90 kPa) and 7.2 ks (2.8 GPa) where t is diffusion time, X diffusion distance from Matano interface.

the diffusion time. In those figures, X and t are converted to Boltzmann parameter for comparison. Diffusion is suppressed by high pressure. Fig. 6 shows an example of a probability plot of diffusion profile of vanadium in the Ni-24.9Al/Ni-22.5Al-1.76V couple as known Hall method [7], where C_i is the concentration of vanadium, C_i^- the terminal zero concentration of vanadium in Ni-24.9Al, C_i^+ the concentration of 1.76 at % V in the terminal composition. We can obtain the impurity diffusion coefficient from the slope of the lower vanadium concentration region.

The pressure dependencies of the impurity diffusion coefficients of platinum, vanadium and manganese are shown in Fig. 7. The activation volume for diffusion can be obtained approximately from [8],

$$\Delta V = -RT(\partial \ln D/\partial P)_T \tag{3}$$

where ΔV is the activation volume, R the gas constant, P the pressure, T the temperature and D the diffusion coefficient. The obtained activation volumes for the impurity diffusion of the three elements in the Ni_3Al phase are shown in Table II. Seeing Table II, diffusion of platinum which substitutes for nickel in the Ni_3Al phase is considered to owe to the monovacancy mechanism [8, 9] because a nickel site has eight nearest neighbour nickel sites. Diffusion of vanadium which substitutes for aluminium sites is considered to owe to the divacancy mechanism [8, 9] or other complex mechanisms. Manganese may diffuse by the both monovacancy and divacancy mechanisms or other complex one such as a six cycle vacancy jump mechanism [10] because manganese occupys both nickel and aluminium sites.

TABLE II Activation volumes ΔV for impurity diffusion of platinum, vanadium and manganese. V_0 is molar volume of Ni_3Al, T diffusion temperature

Specimen	ΔV (m^3/mol)	T (K)	$\Delta V/V_0$
Ni_3Al-Pt	5.1×10^{-6}	1523	0.75
	5.0×10^{-6}	1573	0.75
Ni_3Al-V	7.4×10^{-6}	1523	1.08
	6.6×10^{-6}	1573	0.97
Ni_3Al-Mn	7.1×10^{-6}	1523	1.03
	7.0×10^{-6}	1573	1.01

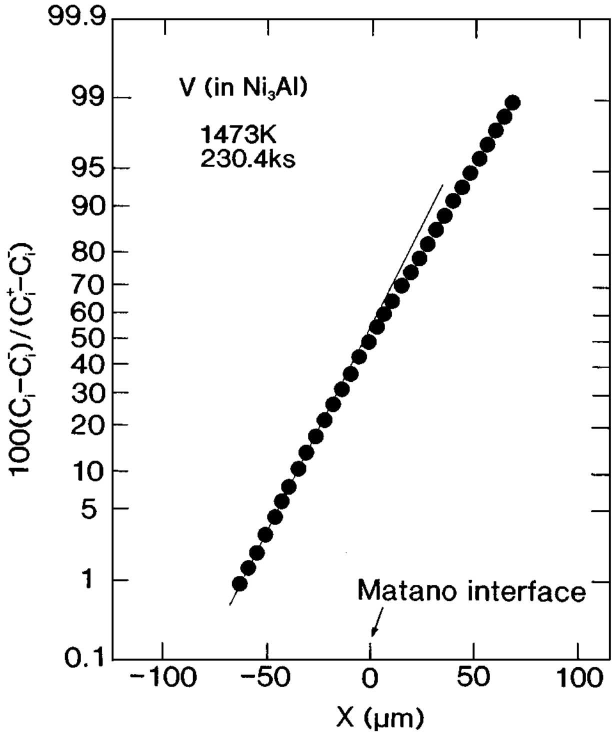

Figure 6 Probability plot of V concentration profile in Ni-24.9Al/Ni-22.5Al-1.76V couple diffusion annealed at 1473 K for 230.4 ks where C_i^+ and C_i^- are terminal compositions of i element ($i = V$) in diffusion couple.

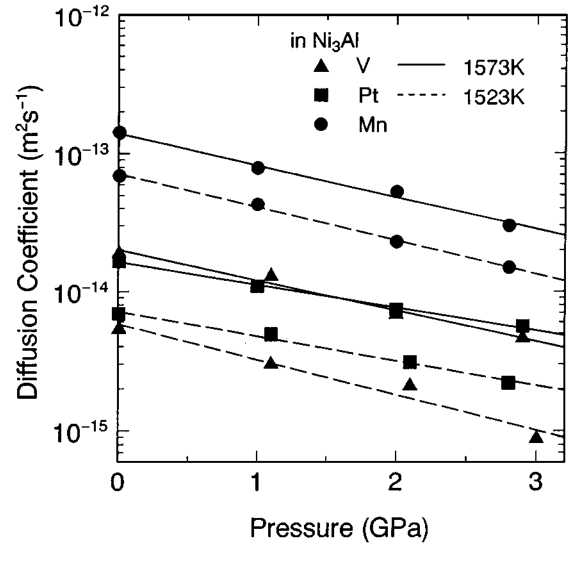

Figure 7 Pressure dependencies of impurity diffusion coefficients of Pt (■), V (▲) and Mn (■) at 1523 and 1573 K respectively.

Fig. 8 indicates the temperature dependencies of the impurity diffusion coefficients of the three elements. The following Arrhenius equations can be obtained from the figure.

For Pt $D = 7.8 \times 10^{-4} \exp(-323\,\text{kJ/mol}/RT)\ \text{m}^2/\text{s}$

V $D = 3.1 \times 10^{-1} \exp(-459\,\text{kJ/mol}/RT)\ \text{m}^2/\text{s}$

Mn $D = 5.9 \times 10^{-1} \exp(-377\,\text{kJ/mol}/RT)\ \text{m}^2/\text{s}$

From the recent theoretical calculation [11], which is based on the pair wise bonding model, we can get the formation energy 158 kJ/mol of a single vacancy of the

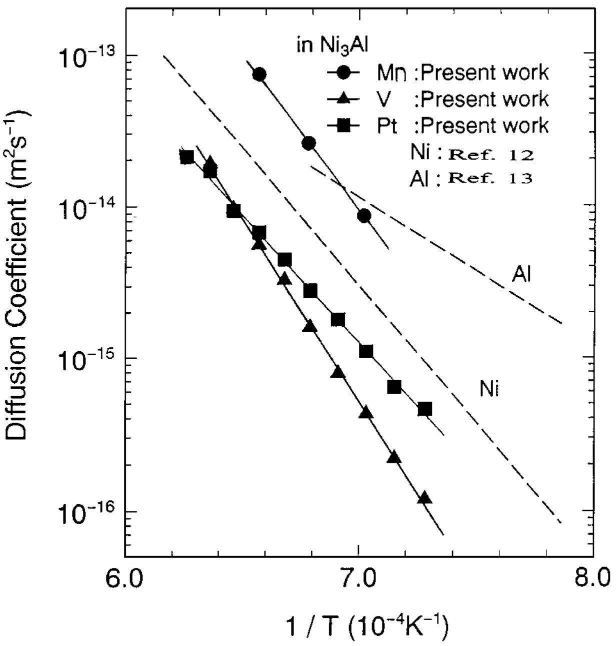

Figure 8 Temperature dependencies of impurity diffusion coefficients of Pt (■), V (▲) and Mn (●) at 90 kPa in Ni_3Al.

α site, and that of the β site 197 kJ/mol. The difference of the formation energies of both sites is about 40 kJ/mol. The platinum atoms occupy the α sites, and vanadium atoms do the β sites. The difference tendency of the activation energies of both elements are similar to 40 kJ/mol, though we must consider the single vacancy migration energy is about 1/3 of that of the formation, and the ordering energy is about 11 kJ/mol.

4. Summary

Impurity diffusion of platinum (α site), vanadium (β site), manganese (α and β sites) are investigated. The obtained activation volumes ΔV to the molar volume of the Ni_3Al phase V_0 are as follows:

$$\text{Pt: } 0.75, \quad \text{V: } 0.97\text{–}1.08, \quad \text{Mn: } 1.01\text{–}1.03$$

Impurity diffusion of the three elements has following Arrhenius relations:

$$\begin{aligned} \text{For Pt} \quad & D = 7.8 \times 10^{-4} \exp(-323\,\text{kJ/mol}/RT)\ \text{m}^2/\text{s} \\ \text{V} \quad & D = 3.1 \times 10^{-1} \exp(-459\,\text{kJ/mol}/RT)\ \text{m}^2/\text{s} \\ \text{Mn} \quad & D = 5.9 \times 10^{-1} \exp(-377\,\text{kJ/mol}/RT)\ \text{m}^2/\text{s} \end{aligned}$$

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